

A ^{13}C , ^2H , ^1H NMR AND GPC STUDY OF STRUCTURAL EVOLUTION
OF A SUBBITUMINOUS COAL DURING TREATMENT WITH TETRALIN AT 427°C
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The recently developed magic angle/cross polarization Waugh-Pines techniques⁽¹⁾ promise to significantly advance the state of understanding of the statistical structure of coals. However, much work remains to be done in the area of detailed product characterization before predictable models of coal reactivity can be constructed. Although tetralin and other donor systems have been utilized in numerous studies, the results of Neavel⁽²⁾ were among the first to demonstrate that certain coals can be rendered soluble in pyridine in >90% conversion in <5 min. Very little effort to characterize the evolution of coal structure over time during reductive thermolysis of coal has been made.

In this work the products from the thermal dissolution of subbituminous Kaiparowitz coal at 427°C in tetralin are examined by spectroscopic (^{13}C , ^1H , ^2H NMR, IR) molecular weight (gel permeation chromatography and vapor pressure osmometry) and elemental analysis and hydroxyl group analysis. The use of 1,1-dideuteriotetralin in conjunction with ^2H NMR to monitor the time dependence of introduction of deuterium into aliphatic and aromatic structures is presented. The tetralin-derived products were monitored versus time by glpc to determine the relationship between hydrogen uptake and coal product yields.

Reactions of Coal and Tetralin or 1,1-dideuteriotetralin

The procedure for these sections is similar to that of Neavel⁽²⁾: A 0.6 cm x 6.3 cm stainless steel tube equipped with threaded caps was charged with 0.15 g tetralin and 0.25 g coal or a 0.95 cm x 6.3 cm tube was charged with 1 g coal and 2 g tetralin. One or more tubes attached to a compressed air vibrator were plunged into a molten lead bath maintained at a temperature which would compensate for the heat uptake by the reaction vessel and stabilized as rapidly as possible at 427°C or 500°C. The sample tubes were withdrawn from the bath at various times from 2.5 min to 2 hr and quenched in water, the contents were washed out with 50 ml of THF and filtered through a 25 μm millipore filter. The insoluble material was dried and weighed. The THF soluble portions were analyzed directly by GPC in THF and the entire reaction mixture analyzed by gas chromatography (GLPC) to determine tetralin, naphthalene, methyl indane et al. The THF solutions were concentrated to 1-3 ml and combined with ~50 ml pentane. The resulting precipitate was repeatedly washed until no tetralin or naphthalene was detectable by GLPC of the pentane wash. This fractionation provides an excellent separation of coal from solvent-derived material. The pentane-insoluble, THF-soluble fractions were examined by vapor pressure osmometry, elemental analysis, GPC, hydroxyl group analysis and ^{13}C , ^2H and ^1H FTNMR.

Results and Discussion

As shown by Figure 1, subbituminous Kaiparowitz coal is rapidly converted to THF-soluble products at 427°C. The ultimate yield of 80% of THF-soluble products plus gases is achieved after approximately 35 min with most (75%) of the ultimate product forming within 10 min. A correction for ash content in the residues would increase the yields by approximately 8%. Vapor pressure osmometry of pyridine solutions of the THF-soluble fraction

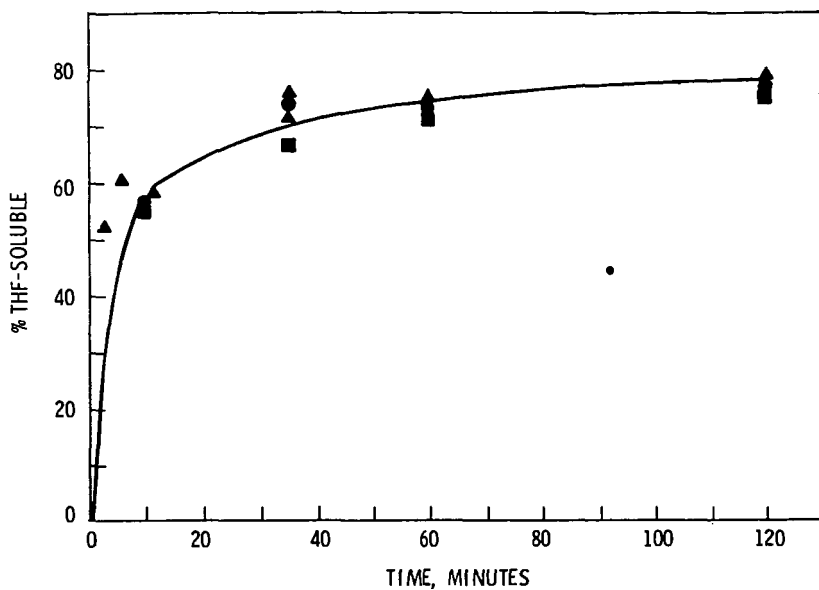


FIGURE 1. Percent THF-Soluble Product plus Gases from 427°C Reaction of Kaiparowitz Coal and Tetralin ■ = Total carbon rendered soluble ● = 1°/sec heatup rate ▲ = 15°C/sec heatup rate

shows a drop in number average molecular weight from approximately 1200 at 10 min to about 500 at 30 min and longer with a slight but reproducible increase after 2 hr reaction. Gel permeation chromatography of the entire reaction mixture in THF (including tetralin and tetralin derived products) shows the molecular size behavior versus time (Figures 2 and 3). Consistent with the vpo results, the principal peak occurs at molecular weight 1000 (polystyrene and polyethylene glycol standards). This peak decreases in size relative to major peaks at MW < 500 so that by 35 min, molecular weights less than 500 dominate weight distribution occur in the first 15-20 min of reaction. After 35 min, the growth of the CA. 300 MW peak occurs only very gradually. The vpo results show an increase in molecular weight from CA. 500 to 600 between 1 and 2 hr. At 500°C the conversion of the higher molecular weight constituents to lower molecular weight products occurs more rapidly than at 427°C. Constituents with MW >10,000 are not observed at 500°C; however, even after 2 hr at 500°C there remains a substantial fraction of material of molecular weight >1000.

The conversion of aliphatic to aromatic structure occurs throughout the reaction. Figure 4 shows the ratio of aliphatic/aromatic hydrogen, deuterium and carbon versus time from integrals corrected for solvent absorptions. The carbon values are not quantitative, but qualitatively exhibit the same trend shown by the proton and deuterium data, with a decrease in C_{ali}/C_{arom} from 0.9 to 0.6 over a 2 hr reaction. The IR spectra of successive THF-soluble fractions shows the expected growth in aromatic CH stretch ($3000-3100\text{ cm}^{-1}$) relative to aliphatic CH stretch ($2900-3000\text{ cm}^{-1}$), and a notable increase in aromatic CH out-of-plane bending motion ($700-850\text{ cm}^{-1}$).

^{13}C NMR spectra for 10, 35, 60 and 120 min reactions were similar in most respects except for small changes in aromatic/aliphatic integrals. The aromatic region of a typical ^{13}C NMR spectrum (Figure 5) revealed a distinct region of absorption at δ 150-160 consistent with aryl ether and phenolic CO and a shoulder at 110-120 ppm, typical of aromatic carbons adjacent to aromatic carbons bearing oxygen atoms.^(3,4,5) The aryl ether and phenolic absorption accounts for 11%, 11%, 7% and 8% of the total aromatic integral of 10, 35, 60 and 120 min reactions, respectively. Since these are quaternary carbons with low or no NOEs, these percentages represent less than half of the actual percentages of aromatic carbons possessing oxygen substituents. Elemental analysis of the THF-soluble fractions (Table 1) reveals a rapid initial drop in oxygen content from CA. 17% in the coal to 14% in the THF-soluble fraction. The %O about 2% over a 2 hr reaction time in the THF-soluble fraction. The percent of oxygen in hydroxyl groups drops from CA. 30% to CA.15% over a 2 hr. reaction time indicating the incursion of dehydrocyclization-type reactions, consistent with the drop in aromatic CO observed by ^{13}C NMR.

Table 1. Elemental Analyses of THF-Soluble Fractions and Coal from the Reaction of 500 mg Tetralin and 250 mg Coal in 0.65 x 6.3 cm Reaction Vessels at 427°C

	Reaction Time,	%C	%H	%N	%S	%O(diff) ^(a)	% ash	%OH ^(b)
	min							
Coal	--	71.0	5.19	1.1	0.3	17.1 ^(a)	8.6	--
	10	75.45	6.19	1.3	0.3	14.0	1.2	4.8
THF-Soluble Fractions	35	76.22	6.32	1.43	0.2	13.9	1.0	4.2
	60	77.81	6.09	1.5	0.3	13.5	0.6	1.8
	120	79.49	6.01	1.7	0.12	13.3	0.8	2.2

(a) Oxygen analyses by difference in the presence of large ash residues are not reliable.

(b) Hydroxyl uncertainty is $\pm 1\%$.

Hydrogen transfer during the reaction is very rapid during the first 15 min of reaction but levels off and becomes sluggish after 30 minutes, after the low energy processes of conversion of coal to preasphaltenes is succeeded by slower bond breaking processes leading to asphaltenes.

The analysis of tetralin, methylindane, and naphthalene by GLPC during the reaction revealed that for every six carbon atoms in the total coal, 1.0, 1.2, 1.7 and 2.4 hydrogen atoms are transferred from tetralin at 5.5, 10, 35 and 60 minutes reaction time. Thus the hydrogen uptake per incremental increase in product yield is much lower in the initial 5 min of reaction than at succeeding times. This is consistent with the breaking of fewer bonds per weight of solvated material yielding radicals or ions which may abstract hydrogen or hydride from tetralin during the early stages of reaction.

The ^2H NMR results⁽⁶⁾ (Figure 4) qualitatively support the concept of a rapid initial disruption of aliphatic structure in the early stages of conversion of coal to preasphaltenes. About 55% of the coal is dissolved within 10 minutes, deuterium incorporation occurring much more rapidly at aliphatic sites.

The ^1H NMR results reveal that the bulk of aliphatic hydrogen occurs at position β to aromatic rings ($\text{ArCH}_2\text{CH}_2\text{CH}_3$) and cyclohexyl or internal methylenes of normal paraffins (δ 1-1.9) and at positions adjacent (α) to aromatic rings ($\text{ArCH}_2\text{CH}_2\text{CH}_3$) (δ 1.9-3.2). Aliphatic hydrogen is detectable in modest amounts assigned to diaryl substituted methylenes (α^2) (δ 3.2 - 4). As shown by Table 2, the percent of α and α^2 hydrogen doubles from 2.5 to 35 min, consistent with a significant increase in aromatic structure during the reaction.

TABLE 2. Distributions of Aliphatic Hydrogen versus Time from ^1H NMR Integrals of THF-Soluble Products (427°C) in Pyridine- d_5

Reaction Time (min)	Chemical Shift Ranges, δ (ppm)			
	δ 0-1.0	δ 1.0-1.9	δ 1.9-3.2	δ 3.2-4.0
2.5	18%	55%	24%	3%
10	13%	48%	34%	5%
35	10%	38%	44%	7%
60	9%	45%	39%	8%

Summary

The dissolution of subbituminous coal occurs very rapidly to produce predominantly phenolic aromatic or aryl ether structures associated with about an equivalent amount of aliphatic structure with molecular weights typically around 1000, and as high as 30,000. The ^{13}C NMR spectra show the products to possess a wide variety of structures in the chemical shift regions of diaryl and triaryl methanes and ethanes, cyclic and acyclic saturated hydrocarbons, with insignificant oxygenated aliphatic, carbonyl or quinoidal structure. Oxygenated aliphatics, if present, are destroyed in the first 10 min of reaction.⁽⁷⁾ The hydrogen transfer process occurs initially at aliphatic sites but is soon incorporated in aromatic structure, as indicated by ^2H NMR results. The ^1H NMR results confirm the gradual production of aromatic structure during the reaction. The incursion of condensation reactions is reflected in a gradual upswing of average molecular weights beyond 1 hr reaction times, as well as a small but definite drop in hydroxyl group content in the coal products.

Acknowledgment

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7. (a) Similar decreased in oxygen content have been reported in experiments using naphthalene or phenanthrene as a reaction medium: Whitehurst, D. D., M. Farcasiu, and T. O. Mitchell, "The Nature and Origin of Asphaltenes in Processed Coals," Electric Power Research Institute Report AF-252, Annual Report, February, 1976, Ch. 10, and references therein. (b) See ibid., p. 6-46 for comments on quinoidal functions.

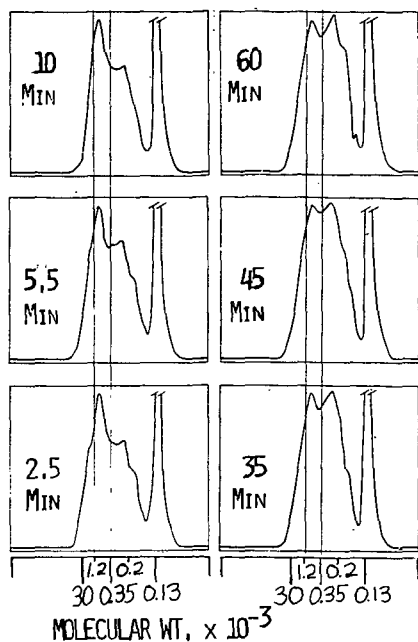


FIGURE 2. GPC trace of the THF solutions of products from the reaction of tetralin and coal at 427°C for varying periods of time. Tetralin and tetralin-derived products appear at MW 130.

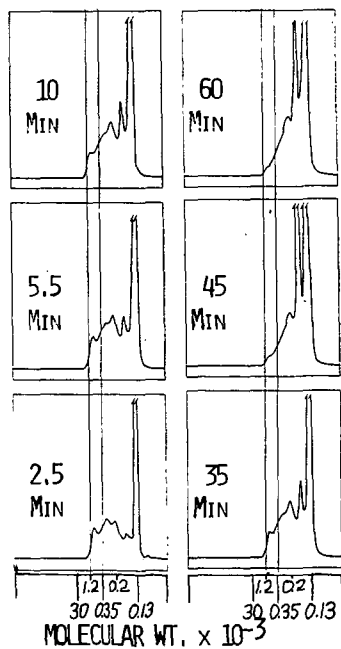


FIGURE 3. GPC trace of the THF solutions of products from the reaction of tetralin and coal at 500°C for varying periods of time. Tetralin and tetralin-derived products appear at MW 130.

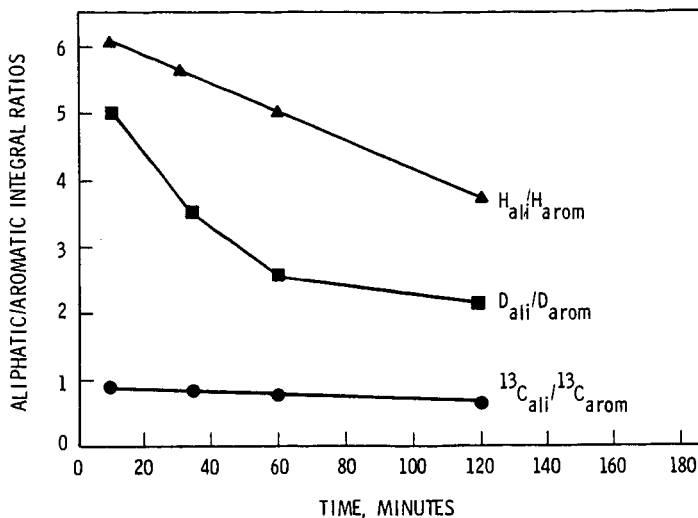


FIGURE 4. Aliphatic/Aromatic FTNMR Integral Ratios vs. Time for Reactions of Coal and Tetralin at 427°C. FTNMR spectra were determined at 79.54 MHz (1H), 20.000 MHz (^{13}C) and 12.211 MHz (2H) with a Varian model FT-80 multinuclear FTNMR spectrometer.

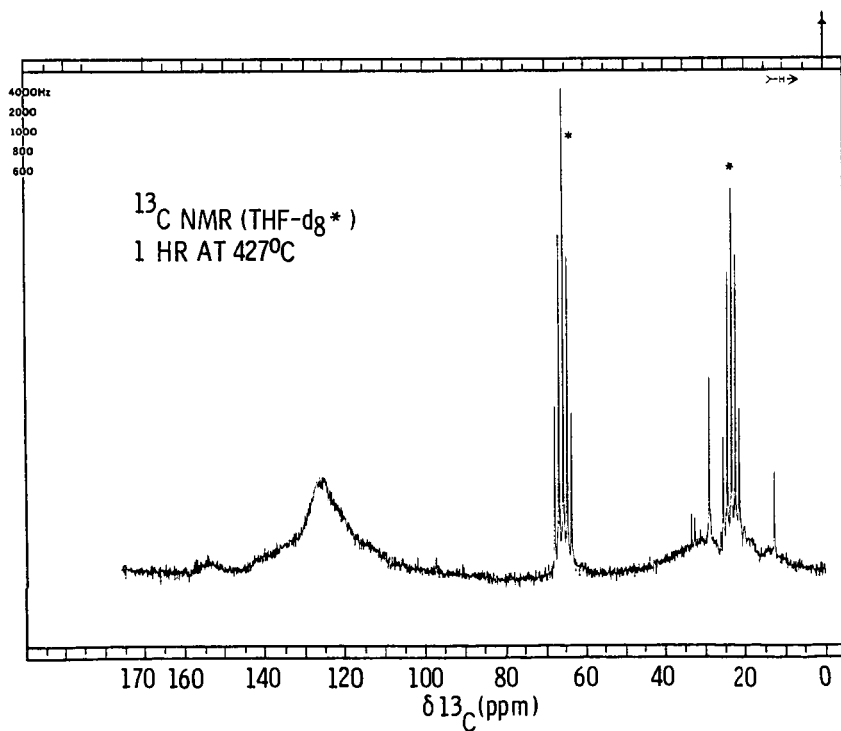


FIGURE 5. ^{13}C FTNMR Spectrum of the Pentane-Insoluble, THF-Soluble Products from the reaction of Tetralin and Coal in THF- d_8 at 427°C for 1 hr.